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Abstract

Because of the increasing interest in urban particle and other modeling and in acid precipitation, the need for stationary source measurement methods for such non-criteria acid pollutants as H_2SO_4 and HCl has also increased. This paper describes several methods for each of these pollutants. Several variations of the temperature controlled condensation method for gaseous H_2SO_4 measurement are described. This method is generally the preferred method for most source measurements. Methods based on the solubility differences of H_2SO_4 and SO_2 in isopropyl alcohol (IPA) and a H_2SO_4 monitor based on the colorimetric measurement of the chloroanilate ions formed when H_2SO_4 is present are reported. Some of the advantages and disadvantages of these methods are also discussed.

Most of the gaseous HCl measurements are made with a sampling train where the HCl is collected in midget impingers containing a NaOH solution. Several analytical procedures for determining the Cl^- concentration, possible interferences in HCl methods, and the use of a remote Fourier transform infrared technique are discussed.

Some field measurements of both gaseous H_2SO_4 and HCl are presented.

Introduction

Early work on stationary source emissions emphasized the measurement of the gaseous pollutants SO_2 , NO and NO_2 . Recently, more attention has been focused on gaseous H_2SO_4 and HCl emissions. These types of measurements are needed for urban particle and other modeling and acid rain studies.

This paper presents several methods for measuring gaseous H_2SO_4 and HCl in source emissions. Separating these pollutants from their ions or precursor which usually exist in much higher concentrations in the emissions is a major problem. In H_2SO_4 methods, SO_2 and $\text{SO}_4^{=}$ must be quantitatively separated from H_2SO_4 . This is especially hard since the SO_2 concentrations are generally 50 times that of H_2SO_4 and the two have very similar solubilities. Similarly, in HCl methods, Cl^- must be separated from HCl . The approaches used to overcome these and other problems will be discussed below.

The sources that emit measurable amounts of H_2SO_4 are those that emit large amounts of SO_2 . With the increased use of the higher sulfur containing fuels, especially those with high trace metal content, the ratio of H_2SO_4 to SO_2 is increasing and H_2SO_4 has become a significant pollutant.

The early concern with gaseous HCl emissions was from the manufacture of hydrochloric acid. However, because of the relatively small amounts of HCl emitted and the generally good tail gas emission controls, these sources are no longer a major concern. The current concern is with the

emissions from incinerators, combustion sources using fuel with high chloride content, and other industries using raw materials with high chloride content such as Portland cement plants. The HCl emissions from the incinerators generally result from the burning of chlorinated polymers, a major component in solid waste. Much of the coal used today has a chloride content ranging up to 0.5%. The average content of 101 US coals reported by Ruch et al¹ was 0.14%. Much of this chloride in coal can be emitted as gaseous HCl.

Methods



Most solvent systems that quantitatively retain H_2SO_4 will also retain SO_2 . The retained SO_2 will generally be slowly oxidized to $\text{SO}_4^{=}$ which is often the substance measured in the method. Flint² investigated the difference in the H_2SO_4 and SO_2 solubility in isopropyl alcohol (IPA) and developed a method based on this solubility difference for measuring SO_3 (H_2SO_4) in the presence of large SO_2 concentrations.

This approach is also used in the U.S. EPA Reference Methods 6 and 8 for SO_2 and H_2SO_4 respectively. In the SO_2 method (Method 6), the emissions after extraction from the source are drawn through a midjet bubbler containing 80% IPA to remove any H_2SO_4 , then through two midjet impingers containing a 3% aqueous H_2O_2 solution for SO_2 collection. The resulting IPA solutions are discarded when the method is followed. However, the method has been modified to measure H_2SO_4 . Dietz³ describes a modified

Method 6 used by the Brookhaven National Laboratory (BNL). The BNL method consists of a sampling train with an isokinetically-sized nozzle assembly containing a quartz fiber filter. The nozzle assembly is followed by a probe that is heated between 175 and 230°C. However, the nozzle assembly containing the quartz filter is only heated by the stack gases. The probe is followed by a series of impingers cooled in an ice bath. The first two units are midget bubblers containing 80% IPA for H_2SO_4 collection with a quartz fiber filter separating the two bubblers. Three midget impingers follow with the first two containing 3% H_2O_2 for SO_2 collection. The final midget impinger is empty and serves as a mist collector.

EPA Method 8 is similar to the BNL modified Method 6. Method 8 measures H_2SO_4 mist and SO_2 in the emissions from H_2SO_4 manufacturing plants. The Method 8 sampling train differs from the BNL train in that Method 8 has no filter in the nozzle, the probe is not heated above 165°C, only the first impinger (not a bubbler) contains IPA, and the impingers are the larger Greenburg-Smith type.

Although IPA is considered not to collect SO_2 , it does retain trace amounts that increase greatly with the presences of any oxidants in the IPA. NH_3 in either the flue gas or the IPA will also increase the SO_2 uptake in the IPA collectors. Dietz³ addressed the oxidant in the IPA problem and suggested a technique to test the IPA for any oxidant. When the H_2SO_4 to SO_2 ratio is high such as in the emissions from H_2SO_4 plants, interference from SO_2 retention in the IPA is minimal. When the ratio is low, this interference can be a serious problem.

Much of the early work with the measurement of the sulfur oxides in combustion source emissions was for corrosion studies. In these studies, the investigators wanted to know the actual H_2SO_4 content, which meant separating the H_2SO_4 from the other sulfates. Goksoyr and Ross⁴ developed a procedure in which the emissions are passed through a filter heated to a temperature that will keep the H_2SO_4 in the gas phase. The H_2SO_4 passing through the filter is condensed and collected in a condensation coil maintained at a temperature below the acid dew point. The particulate sulfate is collected on the heated filter. This method is generally referred to as the temperature controlled condensation method or the acid condensation system (ACS). Cheney and Homolya⁵ studied several parameters of this method and found that the glass frit at the end of the condensation coil tended to retain significant amounts of H_2SO_4 during the sample transfer step. They also found that a temperature between 270 and 280°C (525 to 550°F) minimized the acid retention by the particulate filter. They replaced the condensation coil with a temperature controlled condensation device containing a glass wool plug.

A manual ACS, an automated ACS and a H_2SO_4 monitor made in Great Britain were tested for EPA by Southern Research Institute. The British Severn Science Limited Monitor (SSL) collects the H_2SO_4 in IPA, passes the exposed IPA solution over a porous bed of barium chloranilate and measures the absorbance of the chloranilate ions formed, which indicates the H_2SO_4 content. Dickson⁶ reported that all three methods gave good results. Cheney⁷ miniaturized the ACS for better handling in the field. This micro-acid condensation system (MACS) performed well in field studies.

Gaseous H_2SO_4 can also be measured by infrared absorption. A prototype instrument based on the absorption of gaseous H_2SO_4 at 880 cm^{-1} has been developed for EPA by Laser Analytic⁸. The system uses a tunable diode laser as the 880 cm^{-1} radiation source.

HCL

The first methods for measuring gaseous HCl in emissions from stationary sources were like many of the other gaseous pollutant methods in that the pollutant is collected in a solution with an appropriate sampling train. For gaseous HCl, the collection is made in dilute base usually 0.1N NaOH in midget impingers. The emissions are drawn through a glass lined heated probe with a filtering system if particulate matter is present, through a series of midget impingers, a drying tube, and a pumping system.

In the early testing such as that described in the Public Health Service Document AP-54⁹, a glass wool plug was used to remove the particulate matter. However, the plug has been replaced by flat filters. A good filter that does not retain measurable amounts of the gaseous HCl must be used. Cheney and Duke¹⁰ found that glass fiber filters retained large amounts of HCl, up to 50 times that found in unexposed blank filters. The polymer filters such as Millipore, Nuclepore, and various Teflon filters retained little or no HCl. The results of their study are given in Table I and indicate that glass fiber filters will retain enough HCl to cause a significant error. The midget impinger train consists of two or three midget impingers containing about 15 ml of 0.1N NaOH absorbing solution, an empty midget impinger for droplet removal, and a drying tube. Cheney and Fortune¹¹ reported that a concentration of NaOH as low as 0.01N

gave good results.

Some source emissions also contain measurable amounts of Cl_2 , as well as HCl . The amount of Cl_2 must be determined separately because it will be absorbed in the NaOH solution and measured as HCl . An example of Chlorine present in emissions is in the manufacturing of hydrochloric acid as a by-product of the chlorination of organic compounds, the major method for the production of hydrochloric acid. For these emissions, a second sampling train with alkaline arsenite solution instead of NaOH is run simultaneously with the HCl train. The Cl_2 content is determined by iodimetric titration of aliquots of the exposed arsenite solution. The chloride equivalent from the Cl_2 method is subtracted from the total chloride measured in the aliquots from the HCl train and the difference is reported as the gaseous HCl content.

Chloride ions in the absorbing solution other than those from the HCl will interfere with the analysis. Certain chlorinated hydrocarbons could also interfere. McGaughey et al¹² studied the possible interference of eleven common chlorinated hydrocarbons and found three compounds with significant interference: Chloroform, 1,1,2 trichloroethane, 1,1,2,2 tetrachloroethane. After 18 days, the impingers contained 222, 143, and 139 ppm Cl^- from these compounds respectively. A slight interference was found with 1,2 dichloroethane. The other compounds tested were methylene chloride, carbon tetrachloride, perchloroethylene, 1,1,1 trichloroethane, 1,1 dichloroethane, 1,2 dichloroethane and 2 chloroethyl benzene. The results of the three interfering compounds from this study are given in Table II. In this study, the compounds produced only

negligible amounts of Cl^- in 1 and 3 days exposures. Therefore, to avoid interference from these compounds, the collected samples must be analyzed immediately.

The collected HCl content is determined by either a titration method or ion chromatography (IC). Before IC became available, the Volhard method for Cl^- determination was used. Cheney and Fortune¹¹ have compared four Cl^- titration methods, Volhard, Mohr, Fajans and the mercuric nitrate method. They found that the mercuric nitrate method was superior to the Volhard method because it is simpler to run and gives better reproducibility. The Mohr and Fajans methods gave unacceptable results.

The Cl^- content of the collected samples can also be determined by IC. In laboratories with IC systems, this is generally the preferred method. McGaughey¹² evaluated the use of IC for the HCl methods and found that IC gave very good results.

A chloride specific ion electrode can be used to determine Cl^- content. However, the calibration and running of this procedure is much more difficult and time consuming than either the titration or IC methods.

Gaseous HCl has also been measured in source emissions by a remote Fourier transform infrared spectrometer (FTIR). The spectral region near 2775 cm^{-1} has been used by Herget¹³ to measure gaseous HCl emissions from brick kiln and Portland cement plants. The set-up used by Herget had a sensitivity of about 0.5 ppm. With this system, several other gaseous pollutants such as NH_3 , NO, CO, SO_2 and HF can be measured. However,

it is a costly, unique system that must be operated by highly trained persons.

Results

Table III shows H_2SO_4 concentrations from several sources as determined by different measurement methods. The highest concentration was from an oil-fired utility boiler measured with the BNL modified Method 6. The next highest result was from an oil-fired power plants measured with the ACS method. These sources had average emissions of 39 and 19 ppm respectively. The lowest value of 0.37 ppm was from a recovery furnace at a pulp and paper mill. Values in the range from 1 to 10 ppm are common in sources using fuel containing sulfur and are easily measured by these methods.

The Environmental Sciences Research Laboratory of EPA measured gaseous HCl at coal-fired power plants, incinerators, and Portland cement plants. Some of the results of these studies are given in Table IV. The gaseous HCl found in these emissions ranged from 16 ppm at the Portland cement plant to over 200 ppm at two of the incinerators.

Conclusions

Several reliable methods for measuring gaseous H_2SO_4 and HCl are available. The controlled condensation method for H_2SO_4 is the more widely use method. Good results have been obtained by investigators using a variety of condensation devices and sampling trains. An automated ACS system

has been developed and field tested with good results. A colorimetric monitor made in Great Britain was also field tested and gave good results.

The ACS methods have several potential problems such as maintenance of the proper temperatures on the particulate filter and the condensation device and retention of H_2SO_4 on the glass frit during sample transfer. When a frit is used with a condensation coil, careful rinsing must be employed. With IPA methods, the IPA must be of high quality with no oxidants and the emissions should have only minimal amounts of NH_3 . When a particulate filter is used with this method, some gaseous H_2SO_4 will probably not be recovered.

Certain chlorinated hydrocarbons, Cl_2 , Cl^- can interfere with the gaseous HCl methods. Appropriate corrective measures are known for these potential problems.

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Field Tests
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Acid Pollutants

TABLE I. RETENTION OF GASEOUS HCL BY PARTICULATE FILTERS ($\mu\text{g Cl}^-$)

Filter Type	3 min Samples (1)		1 min Samples (1)		Blanks(2)	
	$\bar{X}$	σ	$\bar{X}$	σ	$\bar{X}$	σ
Glass Fiber	574	60	449	74	8.9	3.7
Millipore	9.0	9.5	14.3	8.8	16	11
Nuclepore	2.9	1.0	1.5	1.3	0.43	0.57
FS(3)	3.6	1.3	3.9	2.5	0.47	0.58
TE(3)	4.5	1.7	2.6	1.2	2.2	1.3
GHIA(3)	3.4	1.1	1.9	1.2	0.13	0.06

¹Average of three runs at $0.0226 \text{ Nm}^3/\text{min}$ with 1500ppm(v/v) HCl in N_2

²Average from three blanks

³Teflon filters

TABLE II. CHLORINATED HYDROCARBON INTERFERENCE IN GASEOUS HCL METHODS

Compounds	Cl ⁻ in impinger after 18 days, ppm
Chloroform	222
1,1,2 Trichloroethane	143
1,1,2,2 Tetrachloroethane	139

TABLE III. H₂SO₄ EMISSIONS FROM SELECTED SOURCES

Source category	Methods	H ₂ SO ₄ Emissions (ppm/v/v)	References
Oil-fired Power Plant	ACS	19.4	-
Recovery Furnace	ACS	0.37	14
Recovery Furnace	ACS	1.54	14
Coal-fired Power Plant Before Scrubber	SSL	11.6	6
Coal-fired Power Plant After Scrubber	SSL	4.4	6
Oil-fired Utility Boiler No Precipitator	BNL	39.3	3
Oil-fired Utility Boiler After Precipitator	BNL	12.2	3
Oil-fired Small Boiler	MACS	2.84	15
Oil-fired Small Boiler	MACS	3.01	15

TABLE IV. GASEOUS HCL EMISSIONS FROM SEVERAL SOURCES

Sources	Size	Average HCl Emission ppm(v/v)	References
Coal-fired Power Plant	100Mw	44.7 $\pm$ 3.8	11
Coal-fired Power Plant	330Mw	23.7 $\pm$ 9.0	11
Incinerator	16 tons/hr	85 $\pm$ 50	11
Incinerator	30 tons/hr	214 $\pm$ 64	11
Incinerator	17 tons/hr	234 $\pm$ 100	16
Portland Cement	120 tons/hr	18 $\pm$ 2 ¹	17
		16 ²	13

¹sampling train method²FTID method